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Canaigre Investigations

Countercurrent Stationary Vat Leaching of Shredded Canaigre Roots

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INTRODUCTION

In recent years, there has been much interest in developing new domestic sources of vegetable tanning materials. The need for tannin in this country and the reasons for the decline in domestic production have been discussed rather thoroughly by Rogers and Russell [8]. In this Bureau emphasis has been placed on extraction of tannin from roots of canaigre (*Rumex hymenosepalus* Torr.), which grows wild in New Mexico, Arizona, Texas and California and which can be cultivated on marginal land. Tannin was extracted from canaigre on a commercial scale as early as the eighteen nineties [4] but because of economic problems and the difficulty of obtaining a steady supply of roots its commercial manufacture was discontinued.

When freshly dug, canaigre roots contain 65 to 75 per cent moisture. The tannin content* and purity (ratio of tannin to soluble solids†) depend on the strain and the conditions under which the plant is grown. On a dry basis the tannin content ranges from 20 to 35 per cent and the purity from 40 to 65. In general, strains with roots having reddish interiors seem to have the higher tannin contents and purities; therefore this strain was used for the experiments. The roots contain considerable starch—about 20 per cent on the dry basis.

In commercial practice, tannin is extracted from various barks and woods with hot water in open leach vats or in pressure autoclaves. Leaching canaigre roots, however, is complicated by the starch. To prevent swelling or gelatinization of the starch, which makes the tannin difficult to extract and the liquors practically impossible to clarify economically, comparatively low temperatures must be used. Also, as reported by Cordon, Beebe and Rogers [3], leaching canaigre shreds with water at 60 to 65° C. produced such a compact bed that the flow was seriously restricted and at lower temperatures tannin recovery was low. Beebe, Cordon and Rogers [2] employed a centrifugal filtration method of leaching finely comminuted particles of canaigre with water at 112° F. This procedure, however, necessitated the mechanical handling of solids as well as liquids between each leach, and this would be rather expensive in large-scale processing. Therefore, it was decided to attempt the leaching of large particles of canaigre in standard-type vats, leaving the solid material in the vat for successive leaches until it was completely spent and moving only the liquors progressively from one vat to another, and to use an aqueous solution of an organic solvent as the extractant. Luvisi, Cordon, Beebe and Rogers [6] reported laboratory-scale leaching of canaigre shreds in Reed-Churchill extraction tubes with a 50 per cent acetone-water solution. The present paper describes pilot - scale investigations made concurrently with those just mentioned. It includes studies on permeability of beds of commercial depth and adequate diameter and also investigations of countercurrent leaching of canaigre shreds with dilute aqueous solutions of isopropyl alcohol.

Preliminary Batch Studies on Solvents and Permeability

To determine the practicability of the leaching method, a single glass column 4 inches in diameter and 4 feet high was set up (Fig. 1). The liquor was circulated externally through a heating coil and rotameter by a centrifugal pump. The packed column of roots was supported by a false bottom of wire-mesh screen. To prevent contamination of the tannin liquors with iron, all parts of the apparatus coming in contact with the solution were made of copper, brass, or stainless steel. To avoid compaction of the bed of solids by suction, atmospheric pressure was maintained at the bottom of the column by throttling the flow rate of the pump.

To obtain a bed of canaigre roots that will remain permeable for extraction, the material must consist of uniform shreds with a minimum of fines. Several methods of preparing the fresh roots in such a form for drying were investigated. A sugar beet shredder, which has high capacity, produced material only about 75 per cent of which was shreds, and even these were nonuniform in cross section and contained many thin particles, which buckled and compacted in the leaching tanks. A Kummer shredder, which is relatively inexpensive, produced a material 80 per cent of which was held on an 8-mesh screen but again the shreds were nonuniform. The best method found for preparing uniform shreds was to use a vegetable dicer, which first cuts the roots into uniform slices and then shreds the slices with a set of revolving circular knives. This method produced a material of which 96 per cent was retained by a 7-mesh screen and which consisted of 91 per cent by weight of uniform cossettes 1/8 inch square. Even though this material contained some fines, it did not require any screening and gave a permeable bed for solvent extraction.

In many cases, particularly with roots prepared on the Kummer shredder, the material was screened before extraction even in the small, 4-inch diameter column, because much of this material had been roughly handled, and a considerable amount of fines had been made accidentally. By screening the material, the permeability of the cossettes could be evaluated without interference from these accidental fines. Also when the small column was used,

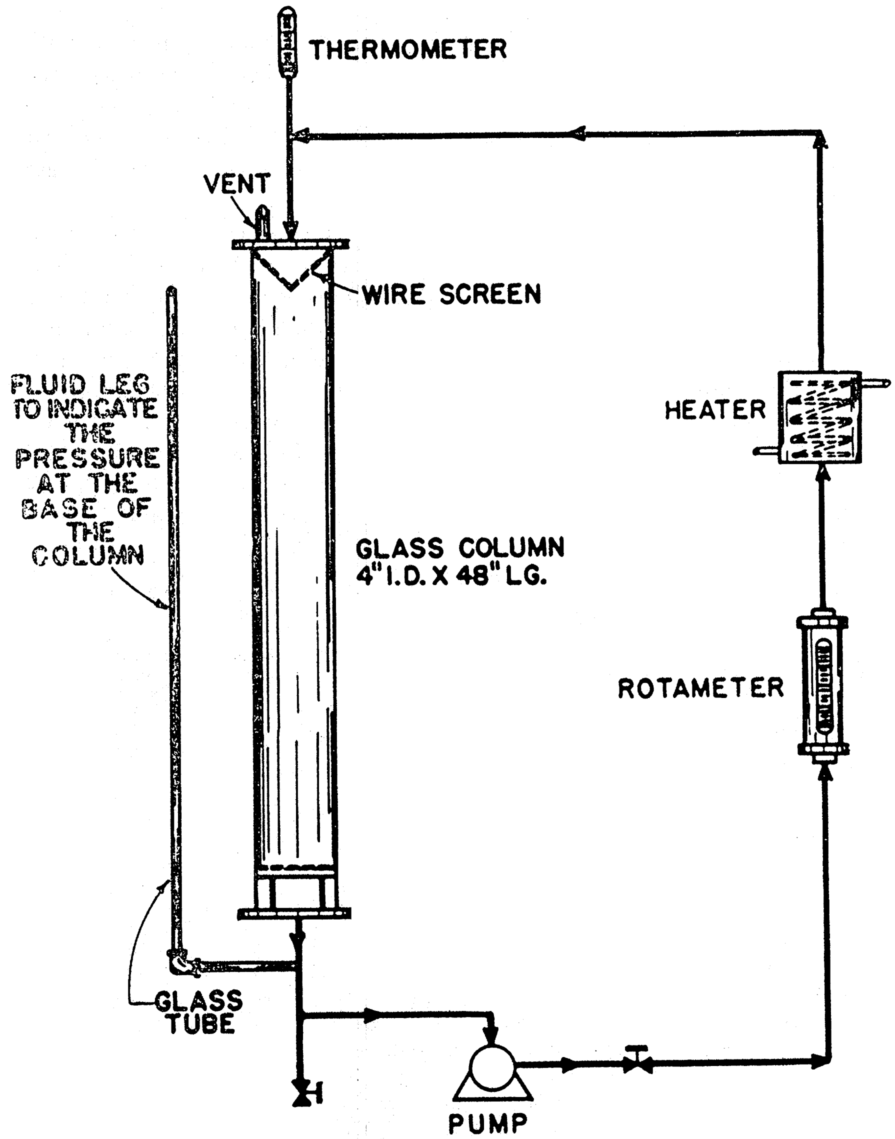

FIGURE 1—Diagram of 4-foot leaching column.

the dried roots were in many instances rehydrated and rechopped to eliminate wall effects. This rechopping would not be necessary in leaching vats of larger diameter.

A number of batch runs were made in which the roots were leached several times; fresh solvent was used for each leach. For one series the solvent was water at 112° F.; for another it was a 25 per cent by volume aqueous solution of acetone at room temperature. Previous investigators had found that both are satisfactory extractants for canaigre tannin [6, 7]. They showed that the temperature of the acetone does not affect the degree of extraction. Acetone would be expected to give a better extraction, but it would increase the cost of processing per pound of raw material. Table I lists the results of these experiments.

Because of the hazard in using acetone and the expense that this hazard would entail, use of isopropyl alcohol was investigated. Small-scale laboratory tests showed that at room temperature, 25 per cent by volume of aqueous isopropyl alcohol extracts canaigre tannin better than warm water but not so efficiently as acetone. Increasing the temperature, however, appeared to increase the solubility of canaigre tannin in isopropyl alcohol solutions; 18 per cent isopropyl alcohol at 112° F. was as effective a solvent as 25 per cent. With acetone, 25 per cent seemed necessary for high extraction, and temperature had no effect. Accordingly, several runs were made with isopropyl alcohol in the small column. Table I also lists these results.

TABLE I

Batch Leaching of Canaigre in 4-Foot Column

Experiment No.	Solvent	Preparation of Roots	Temp., °F.	Number of Leaches	Total Ratio of Solvent-to-Solids	Cumulative Tannin Recovery, %
W12*	Water	Screened on a 7-mesh screen. Hydrated to 58% moisture. Rescreened on a 4-mesh screen	111	4	17	48
C1*	25% acetone	Ditto	83	4	13	81
W13	Water	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 59% moisture.	111	4	16	31
C3	25% acetone	Ditto	80	4	13	63
E3	18% isopropyl	Ditto	111	4	13	65
W14	Water	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 35% moisture. Ground in sharp-knife hammer mill with ½ inch screen. Rehydrated to 60% moisture.	112	7	24	50
C4	25% acetone	Ditto	85	7	21	75
C5	25% acetone	Ditto	79	7	19	71
E1	25% isopropyl	Ditto	79	7	20	62

*Roots used in experiments W12 and C1 were from the same lot; those used in the other experiments were from another lot.

From the first pair of experiments listed in Table I (W12 and C1), it can be seen that cold 25 per cent aqueous acetone gave much better extraction than warm water even when less organic solvent was used. The solvent-to-solids ratio (ratio of total liquid used to original dry weight of solids) was 17 in the water experiment and 13 in the acetone experiment. In all these experiments (Table I), each leach was long enough to make the rate of change of concentration with time extremely small. This meant that in this batch work the first leaches required the longest times. In all the later batch experiments (except C1 and W12, in which all the leaching times were longer), the duration of the first leach was approximately 60 minutes, the second 40 minutes, and the third 30 minutes; and in all succeeding leaches it was 20 minutes. The second set of experiments (W13, C3 and E3) illustrated the same point, although the degree of extraction (recovery of tannin) was different for this lot of roots. They also showed that warm 18 per cent isopropyl alcohol was as good an extractant as the acetone. The third set of results (W14, C4, C5 and E1) again illustrated the increase in extraction with organic solvents and showed that cold 25 per cent isopropyl alcohol was better than warm water but not so good as 25 per cent acetone. The two 25 per cent acetone experiments (C4 and C5) show the effect of a lower solvent-to-solids ratio.

To test the permeability of beds of shredded canaigre of commercial depth, a new column 10 feet high and 9 inches in diameter was constructed (Fig. 2) similar to the 4-foot column. Two batch experiments were made with isopropyl alcohol and acetone under conditions comparable to those used for the experiments in the small column. The roots were shredded in a Kummer shredder with 1/8 inch beet cossette knives before they were dried. After they were dried they were screened through a 2-mesh screen and on a 7-mesh screen. The results of these experiments (Table II) show that extraction in the large column was about the same as in the small column. The slight decrease in recovery in the isopropyl alcohol experiment in the large column was probably due to the lower alcohol concentration used in this run and the lower solvent-to-solids ratio. The permeability of the beds in both these runs was excellent, and by maintaining atmospheric pressure at the bottom of the column in the same way as in the small column, the resistance of the packing never required that the flow be lowered below 1.5 gallons per minute per square foot. The time required for free drainage of liquor over the 10-foot depth was approximately 10 minutes.

Later, an experiment was made with 1/8 by 1/8 inch shreds cut in an Urschel vegetable dicer before they were dried. No fines had to be discarded. With an 18 per cent by volume aqueous solution of isopropyl alcohol as the solvent, the lowest flow (after seven leaches) was 2.5 gallons per minute per square foot and the free drainage time was 10 minutes. With the same material and with water as the solvent, the bed quickly packed down and became almost impermeable. Therefore water was eliminated from consideration as a solvent for this method of extraction.

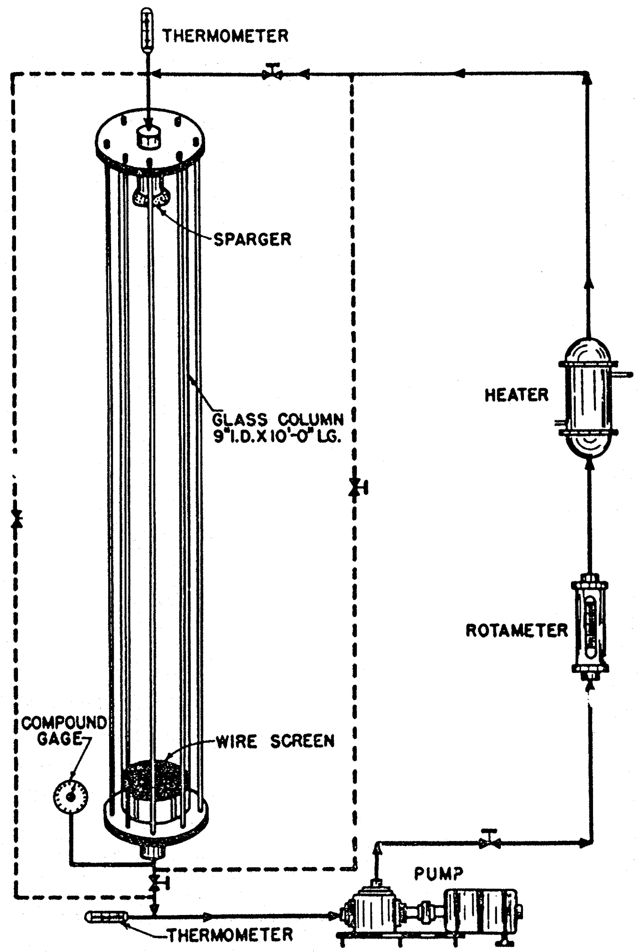

FIGURE 2—Diagram of 10-foot leaching column.

Countercurrent Leaching

To determine recoveries that could be expected in commercial countercurrent operation, a battery of four columns 4 feet deep was constructed (Fig. 3). By drawing off and holding the liquors and, if necessary, the roots, this battery could be used for countercurrent operation with any number of leaches. Figure 4 illustrates the procedure for starting this battery. A batch of roots is put into the first cell (A1, Fig. 4) and is extracted with fresh solvent. This liquor is then discarded. The second batch of fresh solvent is circulated over these partially spent roots (A2) and then over a batch of fresh roots (B1) and is then discarded. This procedure is followed until the required number of cells for the countercurrent extraction are in operation. Then the first

TABLE II

Comparison of Leaching in 4-Foot Column and 10-Foot Column

Experiment No.	Column	Solvent	Preparation of Roots	Temp. °F.	Number of Leaches	Total Ratio of Solvent-to-Solids	Cumulative Tannin Recovery, %
C5	Small	25% acetone	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 25% moisture. Ground in sharp-knife hammer mill with ½ inch screen. Rehydrated to 58% moisture.	79	5	14	65
C9	Large	25% acetone	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 58% moisture.	83	5	15	64
E3	Small	18% isopropyl	Screened through a 2-mesh screen and on a 7-mesh screen. Hydrated to 60% moisture.	111	6	19	72
E4	Large	16% isopropyl	Ditto	112	6	18	67

batch of roots, the most spent, (A6) is removed from the system, the fresh solvent is put on the next batch (B6), and a fresh batch of roots is put on the head end. The battery is run in this manner until the system reaches equilibrium, as indicated by the constancy of composition of the head liquors. Liquors from G1 or H1 are usually close to equilibrium. For tannin extraction, a quick indication of the composition of the head liquor can be obtained by density measurements.

Ten leaches was the largest number used in the countercurrent operation of this apparatus. During each leach, the liquor was circulated for 45 minutes before being transferred to the next batch of roots. The spent material, which had been leached 10 times, was discharged dripping wet and discarded. In commercial practice, the spent material would probably be pressed and the press liquor returned to the system with the fresh solvent. The canaigre used was screened on a 5-mesh screen and rehydrated to 57 per cent moisture with aqueous isopropyl alcohol. The solvent used was 18 per cent by volume aqueous isopropyl alcohol at 112° F.; the solvent-to-solids ratio was 9.2 to 1.

At equilibrium, the last three head liquors contained 81 per cent of the tannin in three batches of fresh roots (shown by analysis). The average tannin content of the last three batches of spent roots corresponded to 9 per cent of the tannin present in the fresh roots. Three liquors and three batches of spent roots were used to determine the recoveries to compensate as much as possible for mechanical losses or surges in the system. The total material balance showed 3 per cent loss, whereas the tannin balance showed a 10 per cent loss. Most of this loss was probably in the mechanical handling of the liquors and would not be nearly so large in large-scale operation. It

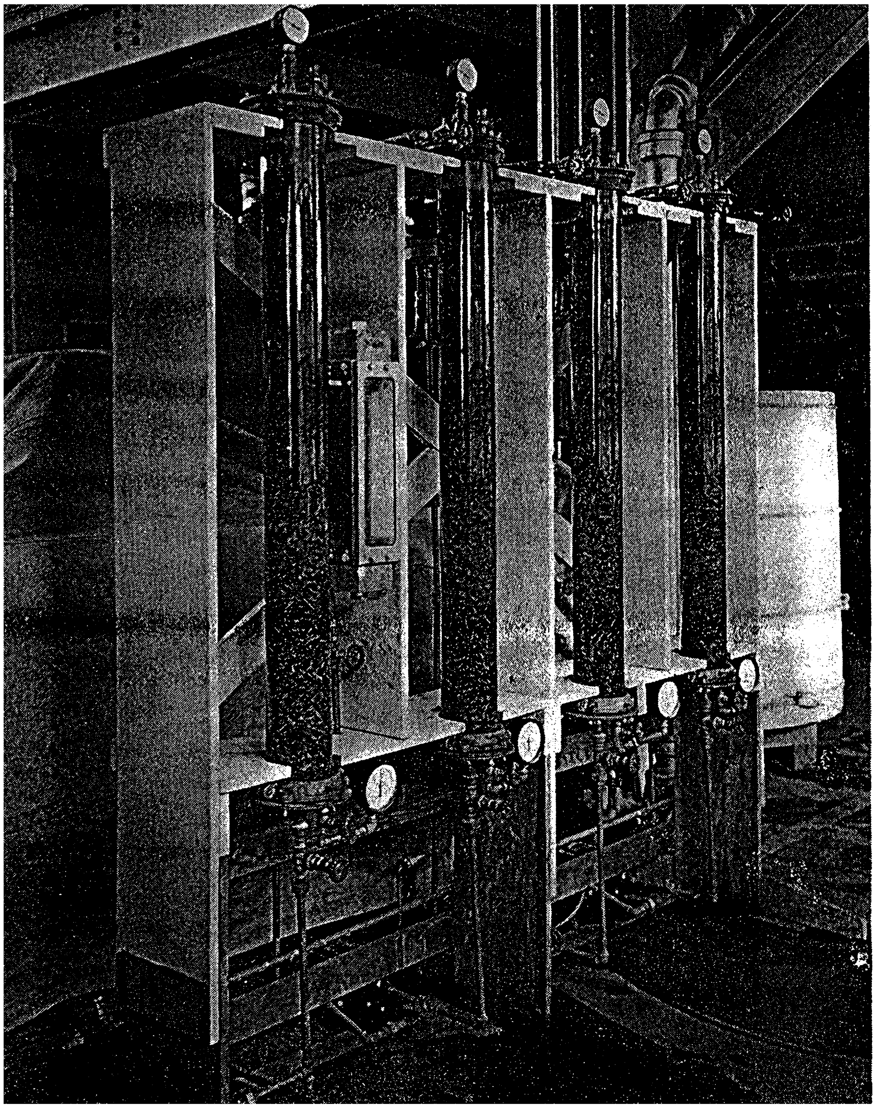

FIGURE 3—Countercurrent Leaching Battery.

is thought, therefore, that these results indicate a potential tannin recovery of somewhat higher than 81 per cent by this method on a commercial scale.

Samples were taken of the liquors in each cell of the battery at equilibrium and were analyzed for tannin content. The tannin recoveries calculated from these analyses are plotted in Figure 5. Also, at equilibrium 1-ounce samples

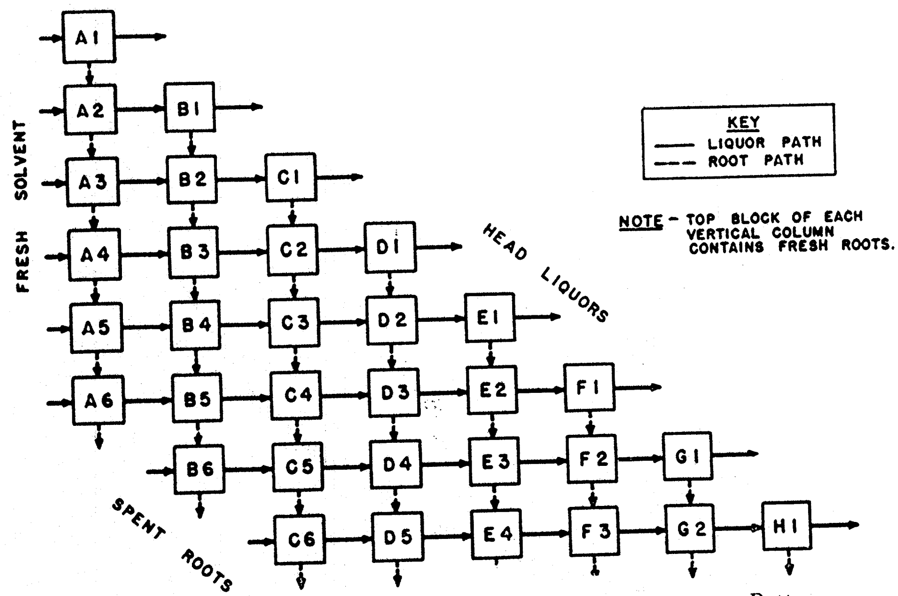

FIGURE 4—Diagram of Procedure for Starting Countercurrent Battery.

were taken in each cell every 5 minutes, and the specific gravity of these samples was measured with a pycnometer to show the approach to equilibrium in each cell. These values are plotted in Figure 6. The last three leaches show no increase in density after 15 minutes, indicating that the 45 minutes chosen for the time of leaching was considerably more than adequate.

The tannin recovery of 81 per cent obtained in this experiment with 10 cells and an 18 per cent solution of isopropyl alcohol shows some improvement over the value of 77 per cent reported by Luvisi *et al*[6] for a 15-cell leach with a 50 per cent solution of acetone. Also the work here reported with the large column indicates that packing and channeling can be avoided in commercial practice by proper shredding. However, both these recovery values are lower than the 90 to 93 per cent recovery obtained by Luvisi *et al*[6] with various solvents, a finer comminution of the roots, and use of a batch slurrying process.

Conclusions

These experiments showed that canaigre roots can be leached in beds of commercial depth without compaction of the bed and restriction of the flow of solvent if the roots are cut in uniform shreds and if a 25 per cent by volume aqueous solution of acetone or an 18 per cent solution of isopropyl alcohol is used as the solvent. The latter solvent is preferred because it is much less hazardous. In this work the roots were cut in a vegetable dicer to uniform

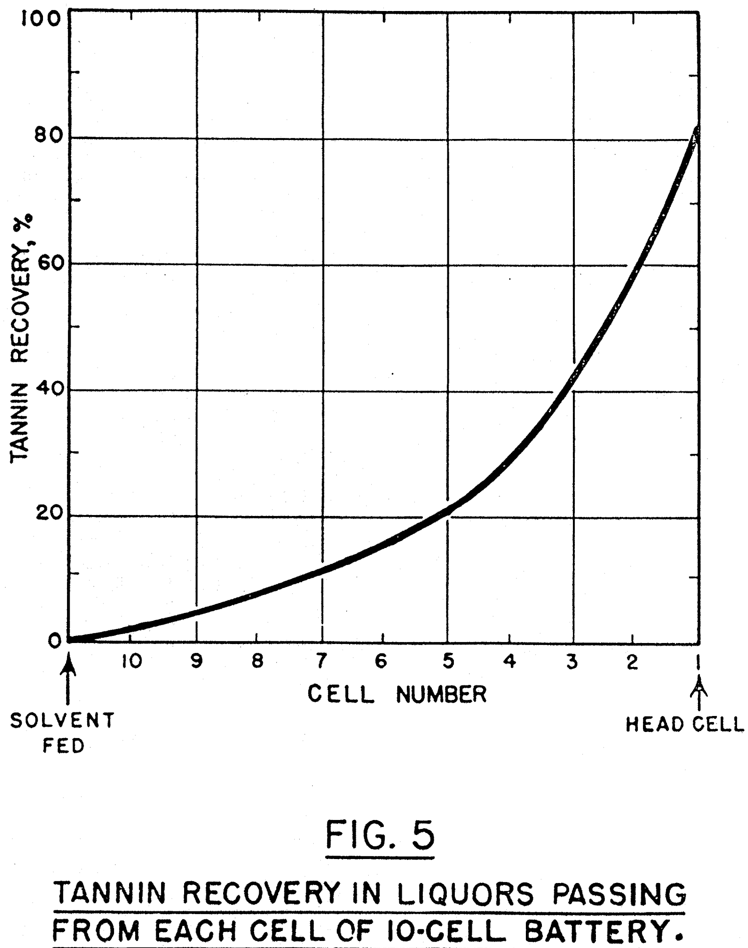

FIGURE 5—Tannin Recovery in Each Cell of a 10-Cell Battery at Equilibrium.

cossettes approximately ⅛ inch square. With roots prepared in this form and a 10 cell stationary vat countercurrent system, a tannin recovery of 81 per cent has been obtained when an 18 per cent by volume aqueous solution of isopropyl alcohol is used as the solvent. Other methods of extraction now being investigated, however, seem to promise higher extraction efficiencies and lower costs per pound of finished tannin.

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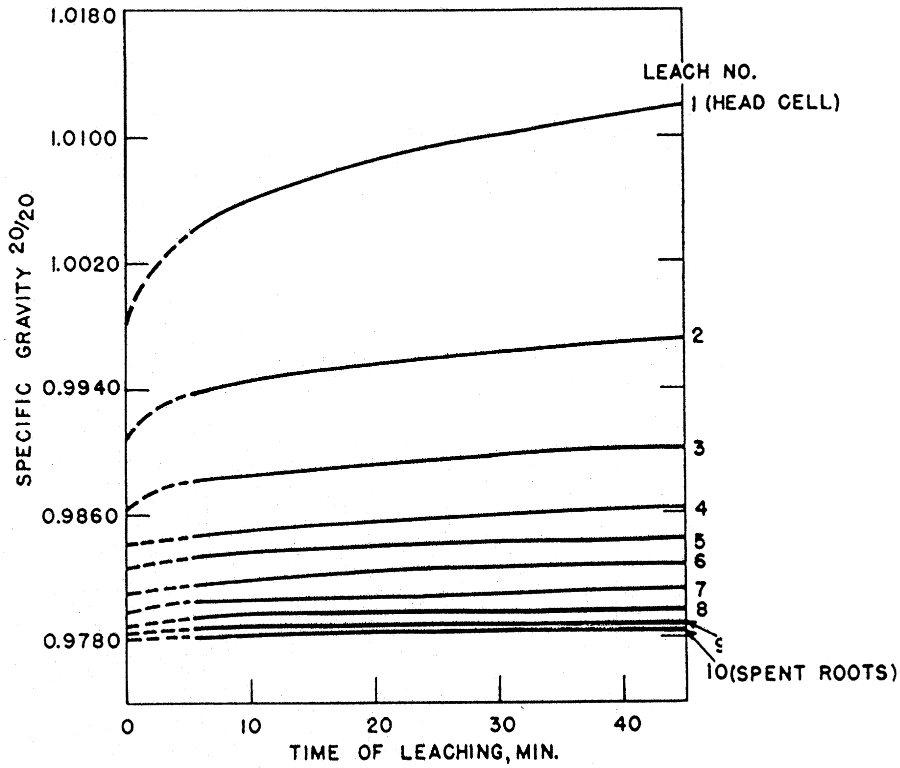

FIGURE 6.—Approach to Equilibrium in Each Cell of a 10-Cell Battery at Equilibrium.

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